UNIVERSITY OF PENNSYLVANIA

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EFFECT OF ADDITION OF ELECTROLYTES

AN ESSENTIAL PORTION OF
A DISSERTATION
IN CHEMICAL ENGINEERING
PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

LEO GARWIN

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Separation of Nickel and Cobalt by Extraction from Aqueous Solution

PRELIMINARY STUDIES

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The use of liquid-liquid extraction as a means of separating the chlorides of nickel and cobalt is considered. The solvent employed in the extraction studies, capryl alcohol, was selected after extensive determinations of the solubilities of the anhydrous salts in a variety of organic compounds. It was found that, although anhydrous cobaltous chloride is soluble in this solvent, little extraction takes place from a simple aqueous solution of the salt. Extraction does take place, however, in the presence of high concentrations of certain added electrolytes. The degree of extraction can be correlated with (1) the intensity of the blue color of the aqueous phase and (2) the magnitude of the activity coefficient possessed by the pure added electrolyte in concentrated aqueous solution. These correlations may be of value in extending the application of liquid-liquid extraction to other inorganic separations. Quantitative data for the extraction of pure cobaltous and nickelous chlorides and 1 to 1 mixtures of the salts from aqueous solution are presented.

THE separation of nickel and cobalt has been one of practical importance to the metallurgical industry for some time. The elements frequently occur together in nature and their separation is not accomplished readily. Because of the differential which exists in the market value of the metals, their separation by a simple process is economically attractive and has evoked considerable interest.

The commercial method of separation most widely employed at the present time involves the treatment of an acid solution of the divalent metal salts with an alkaline solution of an oxidizing agent (*3, 15, 22*). The cobalt is preferentially oxidized and precipitated as the hydrated cobaltic oxide, $Co_2O_3.3H_2O$. A few studies of the conditions for optimum separation by this method have been reported (*36, 44*).

Relatively little attention has been directed toward the possibility of effecting separations of inorganic salts by a liquid-liquid extraction process. The extraction of ferric chloride from hydrochloric acid solution by the ethers has been studied to the greatest extent, particularly in recent years (*1, 7, 20, 29, 30*). Its application to the production of iron-free alumina has been pointed out (*18, 25*). Mass transfer coefficients for the ferric chloride extraction by isopropyl ether in a spray tower have been obtained (*10*). Some literature has appeared on the extraction of uranium, rhenium, and tungsten (*17*), the extraction of certain metallic salts from potable water by acetylacetone (*46*), and the extraction of vanadium from acid solution by isopropyl ether (*19*). It has been found that neither nickelous nor cobaltous chloride is extracted from aqueous solution by the ethers (*7, 11, 27, 28, 41, 45*).

ANALYSIS OF THE PROBLEM

The problem of the separation of two salts in aqueous solution by extraction with an organic solvent resolves itself into: (*a*) the selection of a satisfactory solvent; (*b*) the securing of equilibrium data on the distribution of the salts between the organic and aqueous phases; and (*c*) the determination of mass transfer coefficients in an experimental contacting apparatus.

Once the solvent is chosen, the distribution data are required to predict the performance of equilibrium extraction stages, whereas the mass transfer coefficients, together with the equilibrium data, are needed for the design of true countercurrent extraction equipment operating continuously under steady-state conditions.

SELECTION OF SOLVENT

The suitability of a solvent for a given separation may be expressed in terms of the separation factor, β, equal to the ratio of the distribution coefficients of the solutes between the two liquid phases at equilibrium. Thus, β may be defined as follows:

$$\beta = \frac{K_{Co}}{K_{Ni}} = \frac{[Co]_s}{[Co]_w} \div \frac{[Ni]_s}{[Ni]_w} = \left(\frac{[Co]}{[Ni]}\right)_s \left(\frac{[Ni]}{[Co]}\right)_w \qquad (1)$$

where K = distribution coefficient, concentration in solvent ÷ concentration in water; Co = cobalt salt; Ni = nickel salt; [] = concentration; s = solvent phase; and w = water phase. β is related to the quantity $([Co]/[Ni])_s$ which, for an ideal system of immiscible liquids, may be replaced by the ratio of the solubilities of the anhydrous metal salts in the solvent, $(S_{Co}/S_{Ni})_s$.

However, solutions of the metal chlorides (the particular salts selected for this investigation) in water and in organic solvents are far from ideal. This is indicated by the tendency of the salts to form hydrates and organic solvates. In addition, organic compounds show some mutual solubility with water; this is detrimental to the degree of separation. Further, the extent to which the liquids are mutually soluble is affected by the presence of the salts. As a result, it is clear that the ratio of the solubilities of the anhydrous salts in the solvent provides only a rough measure of the separation factor but may serve adequately as an indication of the relative merit of various solvents for the separation.

It appeared desirable, therefore, to obtain and evaluate solubility data.

Most of the meager information in the literature (*43*) on the solubilities of anhydrous cobaltous and nickelous chlorides in organic compounds concerns solvents completely miscible with water—for example, the lower alcohols, glycol, formic acid, and hydrazine. Some recent work on the separation of a mixture of the monohydrate salts by acetone (*49*) suggested possibilities for the higher ketones. Because of the paucity of available data, it was necessary to undertake a systematic investigation of the solubilities of anhydrous cobaltous and nickelous chlorides in various classes of water-immiscible organic compounds.

SOLUBILITY DETERMINATIONS. The anhydrous salts were prepared from the hexahydrates. The latter were Baker's C.P., analyzed grade, possessing the following significant impurities: 0.10 to 0.15% cobalt in the nickel salt; 0.04% nickel in the cobalt salt. Each of the hexahydrates was first partially dehydrated overnight in an oven at 100° C., the residual material was then pulverized to a fine powder, and the dehydration completed

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overnight in the oven at 120° to 130° C. The anhydrous salts were kept at this temperature until used. This was advisable because of their great tendency to pick up moisture.

The solvents employed were commercially available products. Each was dried over anhydrous sodium sulfate or potassium carbonate overnight and distilled in a small three-ball Snyder column. The fraction possessing a boiling range closest to the literature value was collected and used for the solubility determinations. Two grades of capryl alcohol were among the solvents investigated. A sample of specially purified, ketone-free material was included for comparison with the commercial grade which contains approximately 15% methyl hexyl ketone.

A few grams of the anhydrous salt and about 20 to 25 ml. of the solvent were introduced into a 50-ml. Erlenmeyer flask, the latter stoppered and then placed in a thermostat maintained at 25.0° ± 0.1° C. The thermometer used was checked against one calibrated by the United States Bureau of Standards. The flask was shaken several times a day. The liquid was sampled and analyzed at intervals until a constant value for the concentration of the salt was obtained. With most of the solvents, saturation was reached in a few days. In the case of the alcohols, however, in which the cobalt salt is particularly soluble, several weeks were often required for saturation.

With one mixture, saturation was also approached from the supersaturation side. Excellent agreement was obtained, indicating the probable absence of any systematic error resulting from the failure to attain true equilibrium.

The supernatant liquid was analyzed for its salt content by pipetting a portion into a weighing bottle, evaporating the solvent at a temperature slightly below the boiling point, completing the removal of solvent by overnight heating in an oven at 130° C., and then weighing the anhydrous salt.

Evaporation of those solvents (benzaldehyde and furfural), which had a tendency to polymerize when heated during the evaporation step, was carried out at room temperature under high vacuum, followed by the customary overnight drying in the oven. The solubility values obtained for these solvents are slightly high because of the formation of a small amount of polymer from traces of the solvent retained by the solid after the evacuation period.

No study was made of the nature of the solid phase (or phases) at equilibrium.

Discussion of Results. The solubility data obtained, expressed in weight per cent, are presented in Tables I to IV. The results show that anhydrous cobaltous chloride is soluble in only certain types of organic compounds. If the demarcation solubility value is taken as approximately 1%, then the aliphatic alcohols, ketones, esters, and acids fall into the good solvent category. The salt is insoluble, however, in the ethers and in the hydrocarbons (aliphatic and aromatic, unsubstituted or substituted with chloro- or nitro-groups); it is relatively insoluble in the aromatic ketones and aldehydes. Its solubility in the aromatic ketones is of the same order, however, as that in the aliphatic members of the group of comparable molecular weight.

The good cobaltous chloride solvents appear to have one property in common—namely, the inclusion in the molecule of a polar functional group involving oxygen. It may be that an —OH group is responsible, either actual as in the alcohol and acids, or potential (by enolization), as in the ketones and esters. Such a possibility is strongly suggested by the failure of the oxygen in ethers to possess any solvent action on cobaltous chloride.

Of the types of organic compounds studied, only the lower molecular weight alcohols appear to dissolve anhydrous nickelous chloride to any appreciable extent.

Since both salts are much less soluble in the ketones than in the alcohols, there was obtained, as expected, a lower solubility of each salt in commercial grade capryl alcohol than in the ketone-free material.

There is probably a significant connection between the extremely low solubility of both cobaltous and nickelous chlorides in the ethers and the reported ineffectiveness of these solvents in the extraction of the salts from aqueous solution.

From the standpoint of the anhydrous salt solubility ratio as a measure of the separation factor, the higher alcohols and lower ketones show the greatest promise. In addition to the separation factor, the following criteria also deserve consideration in the determination of the suitability of a solvent for the extraction:

1. The quantity of solvent required for the complete removal of the more easily extracted salt ($CoCl_2$) might be expected to vary inversely with the solubility of the anhydrous salt in the solvent. A high solubility is desirable, therefore, and the alcohols are far superior to the other classes of compounds in this respect.
2. The mutual solubility of the solvent with water should be as low as possible to minimize the blending of properties which results from the solution of one in the other. The effect of such blending is to produce a decrease in the degree of separation. Further, a low solubility of the solvent in water makes unnecessary a solvent recovery or water recycle system. The ketones and lower alcohols show appreciable mutual solubility with water and hence are not as satisfactory as the higher alcohols from this point of view.
3. The solvent should be stable in contact with air and aqueous solutions of electrolytes.

Table I. Solubility of Cobaltous and Nickelous Chlorides in Alcohols at 25° C.

Solvent	Solubility of Anhydrous Salt, G./100 G. Solution		
	$CoCl_2$	$NiCl_2$	$(S_{Co}/S_{Ni})_s$
n-Butyl	34.6	6.1	5.7
n-Amyl	32.2	7.25	4.4
Isoamyl, primary (2-methyl-4-butanol)	29.2	..	...
n-Hexyl	29.0	6.4	4.5
Isohexyl, primary (2-ethyl-1-butanol)	27.3	1.49	18
Isooctyl, primary (2-ethyl-1-hexanol)	26.2	0.74	35
Octyl, secondary (capryl, 2-octanol)			
Commercial	21.3	0.16	130
Ketone-free	22.4	0.26	86

Table II. Solubility of Cobaltous and Nickelous Chlorides in Ketones at 25° C.

Solvent	Solubility of Anhydrous Salt, G./100 G. Solution		
	$CoCl_2$	$NiCl_2$	$(S_{Co}/S_{Ni})_s$
Aliphatic			
Methyl ethyl	2.13	0.01	200
Methyl *n*-propyl	1.20	0.01	100
Methyl isobutyl	0.41	0.01	40
Diethyl	0.53	..	...
Diisopropyl	0.52	..	...
Aromatic			
Acetophenone	0.33	0.05	7

Table III. Solubility of Cobaltous and Nickelous Chlorides in Esters, Acids, and Aldehydes at 25° C.

Solvent	Solubility of Anhydrous Salt, G./100 G. Solution		
	$CoCl_2$	$NiCl_2$	$(S_{Co}/S_{Ni})_s$
Esters (aliphatic)			
Ethyl acetate	1.08	0.02	50
Isopropyl acetate	0.93	0.03	30
Acid (aliphatic)			
Isovaleric (β-methyl butyric)	2.3	0.42	5.5
Aldehydes			
Benzaldehyde (aromatic)	0.29	0.13	2.2
Furfural (heterocyclic)	0.06	0.13	0.5

Table IV. Solubility of Cobaltous and Nickelous Chlorides in Miscellaneous Solvents at 25° C.

Solvent	Solubility of Anhydrous Salt, G./100 G. Solution	
	$CoCl_2$	$NiCl_2$
Ethers (aliphatic)		
Ethyl	0.021 (2)	
Isopropyl	0.01	0.00
Hydrocarbons (unsubstituted)		
n-Heptane (aliphatic)	0.04	0.07
Benzene (aromatic)	0.02	0.03
Hydrocarbons (nitro-)		
Nitromethane (aliphatic)	0.01	0.00
Nitrobenzene (aromatic)	0.02	0.02
Hydrocarbons (chloro-)		
Ethylene dichloride (aliphatic)	0.00	0.04
Chlorobenzene (aromatic)	0.02	0.03

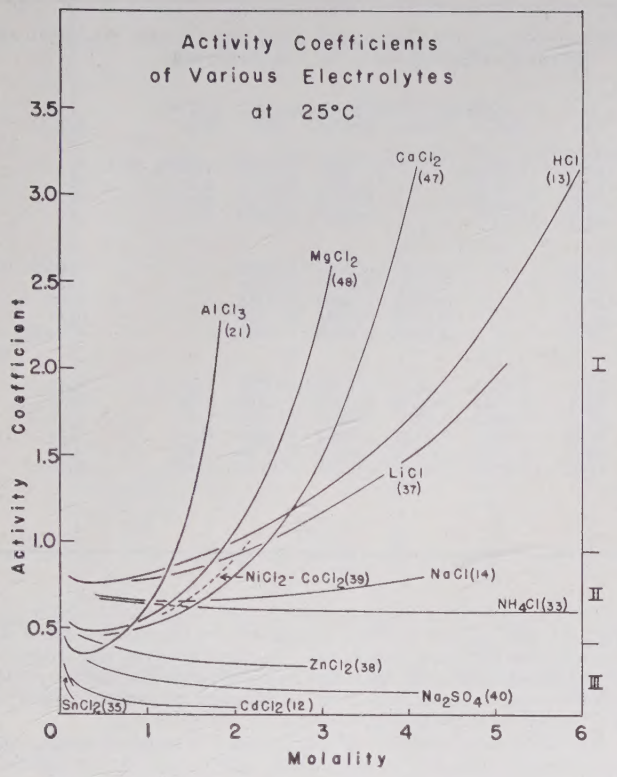

Figure 1

4. The cost of the solvent should be reasonable and it should be available in commercial quantities.

Most of the criteria are satisfied by the higher alcohols. Capryl alcohol was selected for subsequent distribution studies because of the high anhydrous salt solubility ratio in this solvent, the large capacity of the alcohol for cobaltous chloride, its low mutual solubility with water [solubility of capryl alcohol in water: 0.1% (*8*, *26*); solubility of water in capryl alcohol approximately 2.5% (estimated from the trend of solubility with alcohol molecular weight)], its stability, and its availability in tank car quantities at reasonably low cost.

QUALITATIVE DISTRIBUTION STUDIES

Preliminary qualitative experiments yielded the result that cobaltous chloride in dilute aqueous solution is not extracted at all by capryl alcohol; it is only as saturation is approached that the alcohol layer takes on a light blue tint, indicating the presence of some cobaltous chloride. Nickelous chloride did not appear to be extracted regardless of its concentration, for the alcohol phase possessed no color even under conditions of saturation. The solid phase at saturation in each case appeared to be the hexahydrate. This is not surprising, for the stable solid phase at saturation in each salt-water binary system at 25° C. is the hexahydrate (*42*) and the addition of 0.1% of capryl alcohol to the water would not be expected to produce any significant change in properties.

Studies were continued on the effect of the addition of various foreign electrolytes in the belief that the presence of these electrolytes in solution would render the cobalt salt less hydrated and hence make possible its extraction by the alcohol. The results obtained showed that the added electrolytes might conveniently be classified into three main groups:

I. Those such as hydrochloric acid and calcium chloride which produce a gradual color change in the aqueous phase from red through violet to dark blue, the extent of the change depending on the amount of electrolyte added.

II. Those such as sodium and ammonium chlorides which produce a color change to dark red only, even when present to the point of saturation.

III. Those such as sodium sulfate which not only fail to produce a color change from the original red but, in fact, tend to reverse the action of the electrolytes of the other groups. Thus, for example, when added to a solution already turned blue by the previous addition of a group I electrolyte, an electrolyte of this last group causes the solution to become red again.

Considerable attention has been paid to the color changes exhibited by solutions of cobalt salts (*24*). Other electrolytes which have been reported as effecting a color change from red to blue include lithium, magnesium, and aluminum chlorides, whereas such salts as zinc, stannous, and cadmium chlorides have been observed to promote the reverse color change. Of the hypotheses which explain these effects, the complex ion and the hydration theories have received the greatest consideration (*23*).

The qualitative studies produced two correlations: The first involves the intensity of the blue color of the aqueous phase and the degree of extraction of the cobalt by the alcohol. The cobalt was extracted best from dark blue aqueous solutions and not at all when the aqueous phase was red. In the former case the alcohol layer turned blue, in the latter it remained colorless. However, even when the aqueous phase was dark blue, the cobalt was extracted only by such solvents as capryl alcohol and methyl ethyl ketone (solvents in which the anhydrous salt is soluble) and not by the ethers and hydrocarbons (solvents in which the anhydrous salt is insoluble). These facts tend to support the hydration hypothesis, but the latter offers no explanation for the reverse action of such chlorides as cadmium and especially by such a strong dehydrating agent as sodium sulfate.

The second correlation observed was that between the intensity of the blue color of the aqueous phase (and, by the first correlation, the degree of extraction of the cobalt by capryl alcohol) and the magnitude of the activity coefficient possessed by the pure added electrolyte in concentrated aqueous solution.

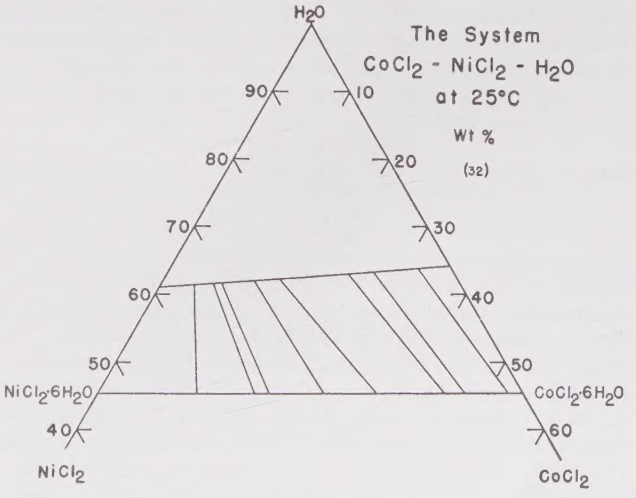

Figure 2

Figure 1 shows the activity coefficients of several electrolytes as a function of concentration. Those electrolytes which produce a marked color change from red to blue (group I) have high activity coefficients in concentrated solution; those which reverse the color change (group III) possess low activity coefficients, whereas those of group II possess intermediate activity coefficient values.

An average activity coefficient curve for nickelous and cobaltous chlorides (whose individual curves are practically identical) is included in the figure. It may be significant that this curve is typical of those shown by the electrolytes of group I.

A possible explanation for the second correlation is that the properties of the added electrolytes in high concentration tend to add to or intensify the properties of the cobalt. Thus, for example, the addition of a group I electrolyte may produce an increase in the cobalt activity coefficient in the aqueous phase and hence an improved distribution in favor of the organic phase; the addition of a group III electrolyte possessing a low activity coefficient in concentrated solution would then be expected to bring about the reverse effect.

TABLE V. DISTRIBUTION OF COBALTOUS AND NICKELOUS CHLORIDES BETWEEN CAPRYL ALCOHOL AND WATER AT 25° C.

Mixture No.	Aqueous Phase					Solvent Phase					
	$CoCl_2$	$NiCl_2$	$CoCl_2/NiCl_2$	$MeCl_2$[a]	Cl[b]	$CoCl_2$	$NiCl_2$	$MeCl_2$[a]	Cl[b]	K_{Co}	K_{Ni}
	Concentration, Wt. %										
Cobalt											
1	35.6	..	..	35.6	19.4	0.0669	....	0.0669	0.0366	1.88×10^{-3}	..
2	33.2	..	..	33.2	18.1	0.0400	....	0.0400	0.0218	1.21	..
3	30.7	..	..	30.7	16.8	0.0207	....	0.0207	0.0113	0.68	..
4	27.6	..	..	27.6	15.1	0.0097	....	0.0097	0.0053	0.35	..
Nickel											
1	..	38.3	..	38.3	20.9	....	0.0716	0.0716	0.0391	..	1.87×10^{-3}
2	..	36.1	..	36.1	19.7	....	0.0446	0.0446	0.0244	..	1.24
3	..	34.4	..	34.4	18.8	....	0.0302	0.0302	0.0165	..	0.88
4	..	32.9	..	32.9	18.0	....	0.0244	0.0244	0.0133	..	0.74
5	..	29.2	..	29.2	15.9	....	0.0098	0.0098	0.0054	..	0.34
Cobalt-Nickel											
1	17.6	19.4	0.91	37.0	20.2	0.0435	0.0254	0.0689	0.0376	2.47	1.31
2	18.7	18.1	1.03	36.8	20.1	0.0421	0.0229	0.0650	0.0355	2.25	1.27
3	17.6	18.1	0.97	35.7	19.5	0.0350	0.0194	0.0544	0.0297	1.99	1.07
4	17.7	17.1	1.03	34.8	19.0	0.0265	0.0173	0.0438	0.0240	1.50	1.01
5	17.8	16.4	1.09	34.2	18.7	0.0254	0.0124	0.0378	0.0206	1.43	0.76
6	15.7	16.3	0.96	32.0	17.5	0.0169	0.0102	0.0271	0.0148	1.08	0.63

[a] $MeCl_2 = CoCl_2 + NiCl_2$.
[b] $Cl = 0.546\ MeCl_2$.

Brdička (*4*), in a polarographic study of red and blue cobaltous chloride solutions, observed a large positive shift in the cathodic deposition potential of the cobalt as its solution is turned from red to blue by the addition of calcium chloride. This shift was interpreted as indicating a considerable increase in the activity of the cobalt ion. However, since irreversible processes are involved in polarographic measurements, true thermodynamic quantities cannot be calculated therefrom, and there is, as yet no direct positive evidence in support of the activity explanation suggested above. The proposed interpretation may nevertheless be valuable in helping to define the optimum conditions for the extraction of an inorganic salt by the proper organic solvent.

The effect of foreign electrolyte addition on the degree of extraction of nickelous chloride by capryl alcohol (in which solvent the anhydrous salt is insoluble) was also qualitatively investigated. No color changes in the aqueous phase were observed in this case; the alcohol layer remained practically colorless, indicating the absence of any appreciable extraction of this solute.

THE SYSTEM COBALTOUS CHLORIDE–NICKELOUS CHLORIDE–WATER–CAPRYL ALCOHOL AT 25° C.

This system was investigated to determine the maximum degree of extraction and separation that could be realized in the absence of any added electrolyte and, further, to study the changes in the distribution coefficient produced by variations in the concentration and by the replacement of one salt by the other. Information regarding the solubility of cobaltous chloride–nickelous chloride mixtures in water is available from the work on the ternary system at 25° C. by Osaka and Yaginuma (*32*). Their results are presented as a triangular plot in Figure 2. These data might be considered to apply to the aqueous phase of the four-component system involving capryl alcohol, for, as mentioned previously, the presence of the alcohol in the aqueous phase to the extent of approximately 0.1% would not be expected to result in any noticeable change in properties.

Figure 2 shows that the system forms a complete series of solid solutions of the hexahydrates and the solubility varies linearly with composition—that is, the strength of a saturated 1 to 1 cobaltous chloride–nickelous chloride mixture is the average of the solubilities of the pure salts. Solid-liquid tie lines are included in the figure.

PURITY OF MATERIALS. The salts employed were the hexahydrates described above. The capryl alcohol used was ketone-free material possessing a refractive index, n_D^{25}, of 1.4260 or higher. The value 1.4264 (*5*) appears to be the most reliable one reported for the pure compound. A small amount was prepared from commercial-grade material by removal of the ketone as the bisulfite addition product. The purification procedure employed was similar to that described (*31*).

ANALYTICAL METHODS. Alcohol phase: A weighed sample was successively extracted with distilled water until free of chloride. The combined extract was then treated as an aqueous phase.

Aqueous phase: The salts were determined by evaporation of a sample to dryness at a temperature slightly below 100° C., followed by complete dehydration overnight at approximately 125° C. The residue was calculated as anhydrous cobaltous chloride, nickelous chloride, or the sum of the two ($MeCl_2$). Such residues are not completely soluble in water. They do dissolve, however, on the addition of a trace of acid, indicating the probable formation of basic salts in the dehydration process. Analytical studies of such residues have been made (*9*, *34*); they show the extent of such basic salt formation to be quite small. Nevertheless, to minimize errors from this source, hydrochloric acid was added to the sample to maintain it on the acid side during the evaporation.

Mixed salt residues were analyzed gravimetrically for nickel content by dimethylglyoxime precipitation. Cobalt was calculated from total salt content by difference. The difference values so obtained were checked in several instances by independent colorimetric cobalt determinations (*16*). The agreement was quite satisfactory. The average deviation was about 1.5%, which is the order of accuracy of the colorimetric method, and no systematic error was evident.

Determinations of the mutual solubility of the capryl alcohol and water in the presence of the salts were not carried out.

PROCEDURE. As has been shown by the qualitative observations described above, detectable extraction from simple aqueous solution takes place only in the region of high concentration. Accordingly, quantitative investigations had to be restricted to the range of concentrations near the point of saturation.

It was decided to make three series of distribution coefficient determinations, one with pure cobaltous chloride, a second with pure nickelous chloride, and a third with both salts in approximately a 1 to 1 ratio in the aqueous phase. In each series the variable factor was to be the total salt concentration.

For the first determination of each series, approximately 150 ml. of capryl alcohol (either fresh or water-washed material from a previous series) and an equal volume of almost saturated cobaltous chloride–nickelous chloride or 1 to 1 mixture of the salts, depending on the series, were introduced into a 500-ml., three-necked flask equipped with a mercury-seal stirrer. The 1 to 1 mixture was prepared by mixing approximately equal volumes of the respective saturated solutions. The flask was placed in a thermostat maintained at 25.0° ± 0.1° C., its contents mechanically agitated for about 5 hours, the phases permitted to separate and a sample of approximately 20 ml. of each phase removed by means of a pipet. Contamination of the lower-phase sample by the upper alcohol phase was prevented by passing a slow stream of air through the pipet as it was lowered through the alcohol phase.

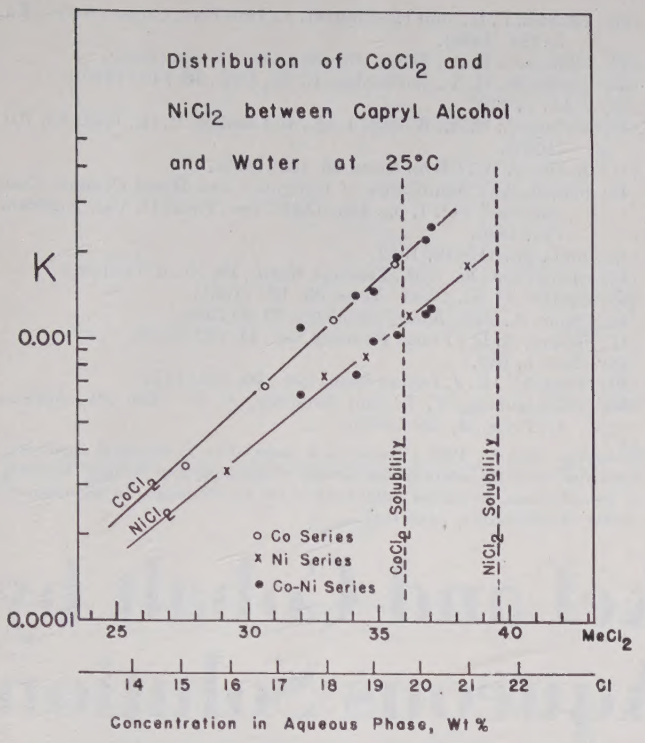

Figure 3

Subsequent determinations in each series were made at progressively lower concentrations by adding a few ml. of water to the mixture from the previous determination and repeating the procedure described above. In the 1 to 1 ratio series, a few determinations were made by the separate mixing of pure salt solutions and not by dilution.

A 5-hour mixing time appeared to be more than ample for the attainment of equilibrium. In one determination, an alcohol phase sample was taken after 1 hour as well as after the usual 5-hour mixing period. The samples, on analysis, proved to be identical. Agitation for 2 to 3 hours has been reported to be sufficient for the reaching of equilibrium in the system lithium chloride–water–isoamyl alcohol (*50*).

Results. The data obtained in the three series of determinations are summarized in Table V. All concentrations are expressed in weight per cent. A semilogarithmic plot of the distribution coefficient against the total chloride (Cl) and total salt ($MeCl_2$) concentrations in the aqueous phase is presented in Figure 3. K is the ratio of the concentration of the salt in the capryl alcohol phase to that in the aqueous phase. $MeCl_2$ represents the sum of $NiCl_2$ and $CoCl_2$. Because the atomic weights of nickel and cobalt differ little, the molecular weights of the chlorides are practically identical and the abscissas in Figure 3 are proportional to one another, regardless of the cobalt-nickel ratio. An average value of 0.546 for the factor $Cl/MeCl_2$ was employed in the computations.

Figure 3 shows that two straight lines, one for each salt species, are obtained. The distribution of each metal salt, whether pure or in a mixture, is a function of the total salt concentration. No satisfactory correlation can be made between K and individual salt concentration.

In spite of the minuteness of the residues and precipitates (2 to 10 mg.) provided by the alcohol phase samples, the results are consistent to a fairly high degree.

The following empirical equations are valid for the region investigated (75 to 100% of saturation):

$$\log K_{Co} = 0.088\,[MeCl_2] - 5.86 = 0.161\,[Cl] - 5.86 \quad (2)$$

$$\log K_{Ni} = 0.083\,[MeCl_2] - 5.90 = 0.152\,[Cl] - 5.90 \quad (3)$$

$$\log \beta = 0.005\,[MeCl_2] + 0.04 = 0.009\,[Cl] + 0.04 \quad (4)$$

In these equations, log represents the Briggsian logarithm and all concentrations refer to the aqueous phase.

Discussion. The variation of the distribution coefficient with concentration is tremendous; there is almost a tenfold change in both coefficients over the limited aqueous concentration range investigated. Even though it is possible to effect some improvement in K_{Co} through an increase in the total salt concentration past the cobaltous chloride saturation limit by means of admixed nickelous chloride, solubility limitations are still responsible for the sudden termination of the trend exhibited by the K's.

Other metal salt-water–organic solvent systems—for example, the systems ferric chloride–water–ethyl ether (*6*) and lithium chloride–water–isoamyl alcohol (*50*)—show a similar marked increase in the distribution coefficient of the salt with increasing concentration, particularly in the dilute range. The K curves in these cases taper off, however, at the higher concentrations.

The dependence of both K_{Co} and K_{Ni} on the total salt concentration only, regardless of the relative salt ratio, illustrates the mutual replaceability of the salts in this respect. This reciprocal effect is not unexpected in view of the general similarity in properties exhibited by the salts.

The results obtained indicate that a separation of nickelous and cobaltous chlorides by extraction from simple aqueous solution with capryl alcohol is not feasible for two reasons: the separation factor is poor, averaging about 1.6; and the distribution coefficient of the more easily extracted salt ($CoCl_2$) is so low (approximately 4×10^{-2} at best) that enormous quantities of solvent would be required for its extraction.

The possibility of raising the temperature to increase the solubility of cobaltous chloride in the aqueous phase and thereby improve its distribution coefficient (assuming no drastic change in the distribution coefficient with temperature) was given consideration. It was felt, however, that the improvement which might result would still be inadequate, and it was decided, instead, to proceed directly to quantitative studies of the degree of extraction and separation obtainable in the presence of group I electrolytes.

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Separation of Nickel and Cobalt by Extraction from Aqueous Solution

EFFECT OF ADDITION OF ELECTROLYTES

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A study of the application of liquid-liquid extraction to the separation of nickelous and cobaltous chlorides is continued with the presentation of equilibrium data on the distribution of the salts between capryl alcohol and water in the presence of hydrochloric acid and calcium chloride. Separation factors ranging from 40 to 90 and from 10 to 17 were obtained with hydrochloric acid and calcium chloride, respectively. The results indicate that either of these added electrolytes may be employed to advantage in effecting a separation of nickel and cobalt by a liquid-liquid extraction process.

QUALITATIVE observations have been described (*6*) which point to an improvement in the extraction of cobaltous chloride from water by capryl alcohol on the addition of certain electrolytes. It has been shown that a correlation exists between the activity coefficient of the added electrolyte in concentrated aqueous solution and the resultant extraction of the cobalt salt. The purpose of this paper is to report the results of quantitative distribution studies with two of the more effective of these added electrolytes, hydrochloric acid and calcium chloride. These particular substances were selected for investigation primarily because their use on a commercial scale would be economically feasible.

COURSE OF THE INVESTIGATION

The study of each five-component system cobaltous chloride–nickelous chloride–added electrolyte–water–capryl alcohol proceeded along lines similar to those originally followed in the investigation of the four-component system cobaltous chloride–nickelous chloride–water–capryl alcohol (*6*). In each case attention was initially directed toward the simpler systems cobaltous chloride–added electrolyte–water–capryl alcohol and nickelous chloride–added electrolyte–water–capryl alcohol. This was succeeded by a study of the complete five-component system.

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A two-phase, five-component system possesses three composition degrees of freedom. If one of these is eliminated by fixing the ratio of two of the components in one phase—for example, by maintaining, as was previously done, the cobaltous to nickelous chloride concentration ratio in the aqueous phase at approximately unity—then such a system is left with the same number of composition degrees of freedom as are possessed by the simpler four-component systems—namely, two. These might be arbitrarily selected as the total salt ($MeCl_2 = CoCl_2 + NiCl_2$) and added electrolyte concentrations in the aqueous phase. It was decided, in any particular series of determinations, to hold one of these constant and determine the effect of variations in the other on the distribution coefficients.

TABLE I. OUTLINE OF SERIES OF DETERMINATIONS WITH HYDROCHLORIC ACID SYSTEMS

(Wt. % concentration units employed throughout)

Series	System	Temp., ° C.	Concentrations in Aqueous Phase: Maintained constant	Varied
(i)	$CoCl_2$–HCl–H_2O–capryl alcohol	25	$CoCl_2$, approx. 10–15%	HCl
(ii)	$NiCl_2$–HCl–H_2O–capryl alcohol	25	$NiCl_2$, approx. 10–15%	HCl
(iii)	$CoCl_2$–$NiCl_2$–HCl–H_2O–capryl alcohol	25	$MeCl_2$[a], approx. 10–15%; $CoCl_2/NiCl_2$, approx. unity	HCl
(iv)		50	Same as for (iii)	HCl
(v)		75	Same as for (iii)	HCl
(vi)		25	HCl, approx. 16%; $CoCl_2/NiCl_2$, approx. unity	$MeCl_2$

[a] $MeCl_2 = CoCl_2 + NiCl_2$.

Accordingly, eleven series of determinations were made, six with hydrochloric acid and five with calcium chloride. Temperatures ranged from 25° to 75° C. The various series are outlined in Tables I and II. Series identical except for the nature of the added electrolyte are similarly designated to facilitate comparison. In Table II the last series of the calcium chloride group,

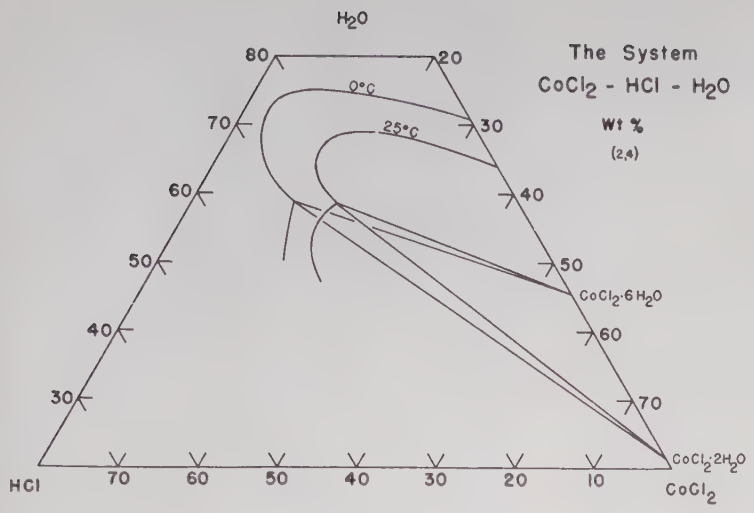

Figure 1

series (v), comprises but a single determination, carried out under conditions of saturation with respect to a solid phase (or phases).

Because the solubility of capryl alcohol in water is low (approximately 0.1% by weight), an aqueous phase in equilibrium with the alcohol possesses properties not very different from those of the pure aqueous solution. It was desirable, therefore, in order to ascertain the concentration limits over which investigations could be carried out without the appearance of a solid phase, to possess a knowledge of the phase behavior of the following systems:

A. $CoCl_2$–HCl–H_2O
B. $CoCl_2$–$CaCl_2$–H_2O
C. $NiCl_2$–HCl–H_2O
D. $NiCl_2$–$CaCl_2$–H_2O
E. $CoCl_2$–$NiCl_2$–HCl–H_2O
F. $CoCl_2$–$NiCl_2$–$CaCl_2$–H_2O

Phase studies have been carried out on the first three of these systems only (*1–4*). The available data are plotted in Figures 1, 2, and 3. Although system *E* has not been investigated, its behavior might be pieced together roughly from Figures 1 and 3 and the results of Osaka and Yaginuma on the system cobaltous chloride–nickelous chloride–water (*7*), reference to which has already been made (*6*).

EXPERIMENTAL

Materials. The nickelous and cobaltous chlorides and capryl alcohol employed for the distribution measurements were of the same purity as the materials used in the preliminary studies (*6*). The added electrolytes, hydrochloric acid and calcium chloride, were Baker's C.P., analyzed grade; the major impurity in the dihydrate crystals of the latter was 0.14 to 0.84% magnesium and alkali salts (as SO_4).

Analytical Methods. The general methods of analysis of the alcohol and aqueous phases for the amounts of nickelous and cobaltous chlorides were the same as previously reported. The hydrochloric acid content was calculated by difference from total chloride and total salt ($NiCl_2$ + $CoCl_2$) determinations on separate samples.

The analysis of calcium chloride in the presence of nickelous and cobaltous chlorides was accomplished by precipitating the metal from an ammoniacal solution with ammonium oxalate and titrating the washed precipitate with standard potassium permanganate. Nickel was determined in the filtrate by dimethylglyoxime precipitation. Cobalt was calculated by difference from a total chloride determination on a separate sample. The reliability of the method was amply demonstrated by test analyses on a series of synthetic mixtures (*5*).

No determinations of the mutual solubility of capryl alcohol and water in the presence of the other components were carried out.

Procedure. The first determination of series (i), (ii), and (iii) was carried out by introducing into the equilibrium flask 150 ml. of capryl alcohol and an approximately equal volume of an aqueous solution of the added electrolyte and either cobaltous chloride, nickelous chloride, or a 1 to 1 mixture of the salts, depending on the series. The flask was placed in a thermostat maintained at 25.0° ± 0.1° C., its contents agitated for about 5 hours, the phases allowed to separate, and 10- to 20-ml. samples removed for analysis.

For subsequent determinations, the aqueous phase sample previously withdrawn was replaced by an approximately equal volume of solution of the same cobaltous chloride, nickelous chloride, or 1 to 1 mixture strength, but more concentrated with respect to the added electrolyte. The agitation, separation, and sampling steps were then repeated. In this manner, the concentration of every component except the added electrolyte was maintained constant in the aqueous phase; the concentration of the latter was progressively increased from determination to determination.

Table II. Outline of Series of Determinations with Calcium Chloride Systems

(Wt. % concentration units employed throughout)

Series	System	Temp., °C.	Concentrations in Aqueous Phase: Maintained constant	Varied
(i)	$CoCl_2$–$CaCl_2$–H_2O–capryl alcohol	25	$CoCl_2$, approx. 6–10%	$CaCl_2$
(ii)	$NiCl_2$–$CaCl_2$–H_2O–capryl alcohol	25	$NiCl_2$, approx. 6–10%	$CaCl_2$
(iii)	$CoCl_2$–$NiCl_2$–$CaCl_2$–H_2O – capryl alcohol	25	$MeCl_2$[a], approx. 6–10%; $CoCl_2/NiCl_2$, approx. unity	$CaCl_2$
(iv)		50	Same as for (iii)	$CaCl_2$
(v)		75	Single determination	...

[a] $MeCl_2$ = $CoCl_2$ + $NiCl_2$.

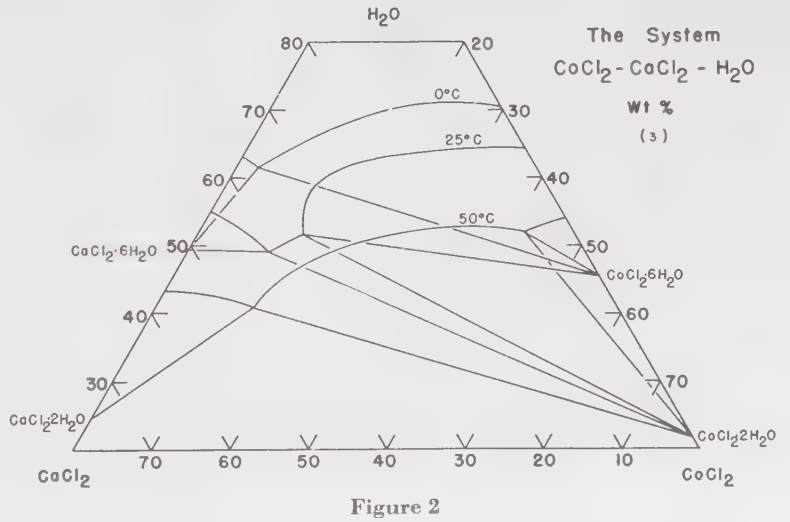

Figure 2

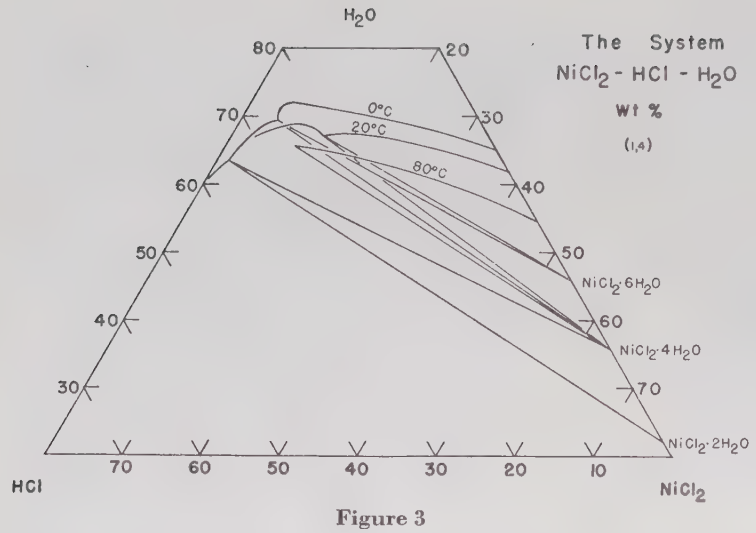

Figure 3

It was found convenient, at the higher calcium chloride concentrations, to add this electrolyte, not in the form of a make-up solution, but as the solid dihydrate. Approximately equal concentration increments could then be obtained over the entire concentration range. The dilution of the mixture in the flask by the addition of the crystals was compensated for by the simultaneous addition of small amounts of the other solutes present.

Small quantities of cobaltous chloride were added at the higher hydrochloric acid and calcium chloride concentrations in series (i) and (iii) to replace the cobalt extracted from the aqueous solution by the alcohol. Addition of nickelous chloride was not necessary in series (ii) as very little of this salt was extracted by the alcohol under any conditions.

Series (iv) and (v) were intended to be comparable with series (iii) in every respect except temperature. The determinations of series (iv) were carried out at 50.0° ± 0.1° C., those of series (v) at 75.0° ± 0.1° C. There was one additional difference when hydrochloric acid was studied. It was deemed advisable to reduce to a minimum the period of time during which systems containing hydrochloric acid were subjected to temperatures of 50° C. or higher. Agitation was allowed for only 3 hours at 50° C. and was reduced to 2 hours at 75° C. Some preliminary work indicated that a 2-hour agitation period was ample for the attainment of equilibrium. These agitation time changes were made because low, erratic results were obtained initially with hydrochloric acid systems continuously exposed to a temperature of 75° C. for 10 days. Alcohol recovered from such mixtures, even after being water-washed and dried, possessed a sharp odor and a dark-brown color. A sample of this material was carefully fractionated. The physical constants and chemical properties of the fractions obtained pointed to the probable formation of 2-chloro-octane as well as octenes. No such action of the added electrolyte on the alcohol was observed when calcium chloride was used.

In series (vi), carried out at 25° C., hydrochloric acid was the only added electrolyte studied. Its concentration in the aqueous phase was maintained constant at approximately 16%. The variable composition degree of freedom in this series was the $MeCl_2$ concentration, which was progressively decreased between determinations by dilution with 16% hydrochloric acid solution. The cobaltous to nickelous chloride ratio in the aqueous phase was again maintained at approximately unity.

Determinations in any particular series were continued until the beneficial effect of further electrolyte addition on the cobaltous chloride extraction became small, as in hydrochloric acid series (i) and (iii) to (v), or a solid phase (or phases) appeared, as in

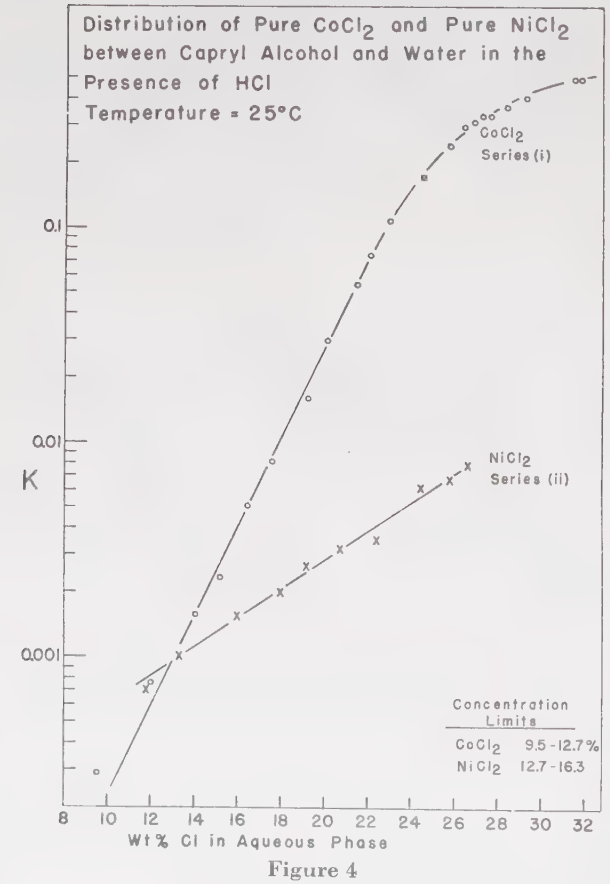

Figure 4

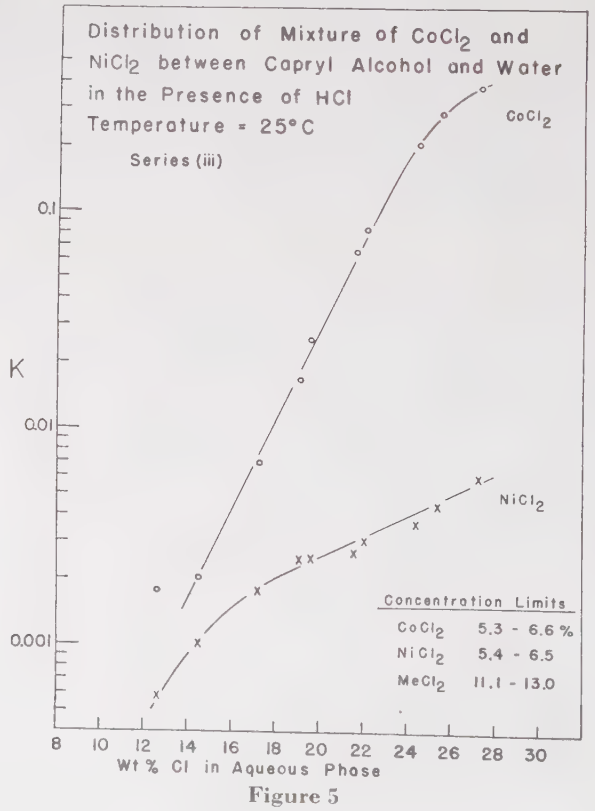

Figure 5

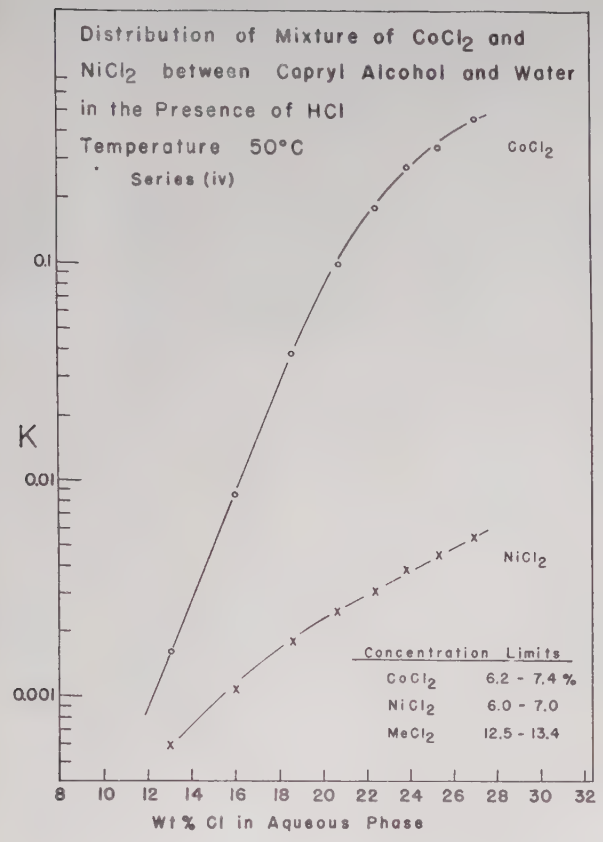
Distribution of Mixture of $CoCl_2$ and $NiCl_2$ between Capryl Alcohol and Water in the Presence of HCl
Temperature 50°C
Series (iv)
$CoCl_2$
$NiCl_2$
K
0.1
0.01
0.001
Concentration Limits
$CoCl_2$ 6.2 - 7.4 %
$NiCl_2$ 6.0 - 7.0
$MeCl_2$ 12.5 - 13.4
8 10 12 14 16 18 20 22 24 26 28 30 32
Wt % Cl in Aqueous Phase

Figure 6

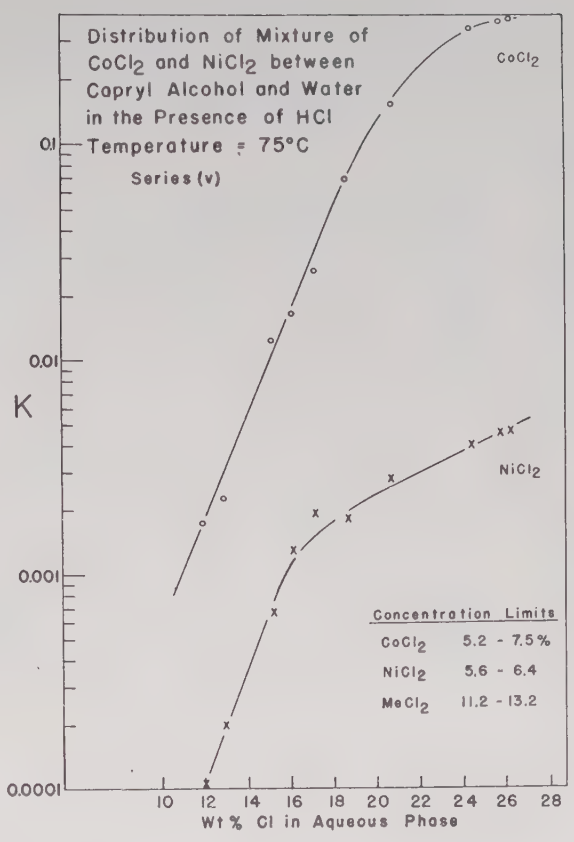

Figure 7

TABLE III. DISTRIBUTION OF COBALTOUS CHLORIDE BETWEEN CAPRYL ALCOHOL AND WATER IN PRESENCE OF HYDROCHLORIC ACID AT 25° C.—SERIES (i)

Mixture No.	Aqueous Phase $CoCl_2$	Aqueous Phase Cl	Aqueous Phase HCl	Solvent Phase $CoCl_2$	Solvent Phase Cl	Solvent Phase HCl	K_{Co}	K_{HCl}
	Concentration, Wt. %							
Co-H								
1	11.6	9.7	3.5	0.0034	0.384	0.393	0.29×10^{-3}	0.112
2	11.9	12.1	5.8	0.0079	1.143	1.17	0.66	0.202
3	12.2	14.0	7.5	0.0183	2.06	2.11	1.50	0.282
4	12.3	15.3	8.8	0.0274	2.81	2.88	2.23	0.329
5	12.1	16.4	10.1	0.0612	3.61	3.68	5.06	0.364
6	11.7	17.5	11.4	0.0976	4.42	4.50	8.35	0.395
7	11.3	19.1	13.3	0.1905	5.09	5.13	1.68×10^{-2}	0.398
8	11.2	20.1	14.4	0.343	5.77	5.75	3.06	0.400
9	11.7	21.4	15.4	0.642	6.59	6.41	5.48	0.416
10	11.0	22.0	16.5	0.787	7.00	6.76	7.15	0.410
11	10.8	23.0	17.6	1.189	7.90	7.47	1.10×10^{-1}	0.424
12	10.2	24.5	19.4	1.795	8.95	8.19	1.76	0.422
13	10.1	25.6	20.6	2.42	9.85	8.77	2.40	0.425
14	9.85	26.4	21.6	2.89	10.51	9.19	2.94	0.425
15	11.2	26.7	21.2	3.65	10.97	9.24	3.26	0.435
16	9.53	27.2	22.6	3.24	11.22	9.73	3.40	0.430
17	11.7	27.7	21.9	4.01	11.72	9.80	3.43	0.447
18	10.5	28.1	23.0	4.02	12.20	10.30	3.82	0.448
19	12.3	29.1	23.0	5.10	12.71	10.20	4.15	0.444
20	11.9	31.3	25.5	5.86	14.30	11.42	4.93	0.448
21	12.7	31.6	25.4	6.25	14.77	11.69	4.92	0.460

TABLE IV. DISTRIBUTION OF NICKELOUS CHLORIDE BETWEEN CAPRYL ALCOHOL AND WATER IN PRESENCE OF HYDROCHLORIC ACID AT 25° C.—SERIES (ii)

Mixture No.	Aqueous Phase $NiCl_2$	Aqueous Phase Cl	Aqueous Phase HCl	Solvent Phase $NiCl_2$	Solvent Phase Cl	Solvent Phase HCl	K_{Ni}	K_{HCl}
	Concentration, Wt. %							
Ni-H								
1	14.2	11.8	4.1	0.0100	0.883	0.90	0.71×10^{-3}	0.220
2	14.2	13.4	5.8	0.0145	1.722	1.76	1.02	0.309
3	13.9	16.0	8.6	0.0223	3.14	3.22	1.60	0.374
4	16.3	17.9	9.3	0.0331	4.26	4.36	2.03	0.470
5	15.7	19.2	10.9	0.0424	5.13	5.25	2.70	0.482
6	16.3	20.7	12.1	0.0529	6.07	6.20	3.24	0.512
7	15.4	22.3	14.3	0.054	7.10	7.27	3.51	0.508
8	14.4	24.3	16.9	0.093	8.46	8.65	6.46	0.511
9	13.9	25.8	18.7	0.095	9.92	10.15	6.84	0.543
10[a]	12.7	26.6	20.2	0.101	10.62	10.85	7.95	0.538

[a] Solid phase present.

hydrochloric acid series (ii) and calcium chloride series (i) to (v), or the concentration of nickelous chloride in the alcohol phase fell to a point where accurate analysis was not possible. This was the case in hydrochloric acid series (vi).

In calcium chloride series (iii), two determinations at saturation were carried out, the equilibrium being approached from opposite directions. Two consecutive determinations at saturation were made with this system at 50° C.—series (iv); the second mixture, as usual, resulted from the addition of calcium chloride to the first.

RESULTS

The distribution data obtained are summarized in Tables III to XII. Semilogarithmic plots of the cobaltous and nickelous chloride distribution coefficients against the total chloride concentration in the aqueous phase are presented in Figures 4 to 11. This particular abscissa was selected in place of the actual variable studied to reduce the tendency of the points to scatter as a result of minor variations in the constant composition degree of freedom.

The appearance or absence of solid phases during the course of hydrochloric acid series (i), calcium chloride series (i), and hydrochloric acid series (ii) was accurately predicted by Figures 1 to 3. Aqueous phase compositions in the first of these series skirted the 25° C. solubility envelope of Figure 1 and no solid phase was encountered. Solid phases were obtained at the termination of the other two series, however, and their final aqueous phase compositions

TABLE V. DISTRIBUTION OF COBALTOUS AND NICKELOUS CHLORIDES BETWEEN CAPRYL ALCOHOL AND WATER IN PRESENCE OF HYDROCHLORIC ACID AT 25° C.—SERIES (iii)

Mixture No.	Aqueous Phase: $CoCl_2$	$NiCl_2$	$CoCl_2/NiCl_2$	$MeCl_2$[a]	Cl	HCl	Solvent Phase: $CoCl_2$	$NiCl_2$	$MeCl_2$	Cl	HCl	K_{Co}	K_{Ni}	K_{HCl}
	Concentration, Wt. %						Concentration, Wt. %							
Co-Ni-H														
1	6.04	6.13	0.99	12.17	12.6	6.1	0.0109	0.0036	0.0145	1.42	1.45	1.81×10^{-3}	0.59×10^{-3}	0.239
2	6.13	6.14	1.00	12.27	14.5	8.1	0.0129	0.0065	0.0194	2.49	2.55	2.10	1.06	0.317
3	6.22	6.40	0.97	12.62	17.1	10.5	0.0435	0.0116	0.0551	4.00	4.08	6.99	1.81	0.389
4	5.69	6.20	0.92	11.89	19.1	13.0	0.0965	0.0155	0.112	5.10	5.19	1.69×10^{-2}	2.50	0.399
5	6.21	6.51	0.95	12.72	19.6	13.0	0.1621	0.0166	0.1787	5.51	5.56	2.62	2.55	0.427
6	5.67	6.44	0.88	12.11	21.6	15.4	0.375	0.0176	0.393	6.69	6.68	6.62	2.74	0.434
7	6.59	6.42	1.02	13.01	22.0	15.3	0.555	0.0200	0.575	7.10	6.98	8.43	3.12	0.456
8	5.27	5.82	0.90	11.09	24.3	18.8	1.106	0.0216	1.128	8.85	8.46	2.10×10^{-1}	3.72	0.450
9	6.33	5.68	1.11	12.01	25.4	19.3	1.819	0.0256	1.845	9.90	9.14	2.87	4.51	0.474
10	6.21	5.45	1.14	11.66	27.3	21.5	2.42	0.0335	2.45	11.17	10.10	3.90	6.15	0.470

[a] $MeCl_2 = CoCl_2 + NiCl_2$.

TABLE VI. DISTRIBUTION OF COBALTOUS AND NICKELOUS CHLORIDES BETWEEN CAPRYL ALCOHOL AND WATER IN PRESENCE OF HYDROCHLORIC ACID AT 50° C.—SERIES (iv)

Mixture No.	Aqueous Phase: $CoCl_2$	$NiCl_2$	$CoCl_2/NiCl_2$	$MeCl_2$[a]	Cl	HCl	Solvent Phase: $CoCl_2$	$NiCl_2$	$MeCl_2$	Cl	HCl	K_{Co}	K_{Ni}	K_{HCl}
	Concentration, Wt. %						Concentration, Wt. %							
Co-Ni-H														
11	6.36	6.78	0.94	13.14	13.0	6.0	0.0104	0.0040	0.0144	1.00	1.02	1.64×10^{-3}	0.59×10^{-3}	0.169
12	6.58	6.83	0.96	13.41	16.0	8.9	0.0567	0.0076	0.0643	2.51	2.54	8.62	1.11	0.286
13	6.24	6.97	0.90	13.21	18.5	11.6	0.237	0.0125	0.250	4.17	4.14	3.80×10^{-2}	1.80	0.358
14	6.45	6.86	0.94	13.31	20.6	13.7	0.650	0.0174	0.667	5.65	5.44	1.01×10^{-1}	2.54	0.397
15	6.66	6.72	0.99	13.38	22.4	15.5	1.218	0.0219	1.240	7.08	6.58	1.83	3.26	0.424
16	6.52	6.29	1.04	12.81	23.8	17.3	1.825	0.0250	0.850	8.15	7.34	2.80	3.98	0.424
17	7.36	5.97	1.23	13.33	25.2	18.4	2.58	0.0274	2.61	9.18	7.98	3.50	4.60	0.433
18	6.20	6.30	0.98	12.50	26.9	20.6	2.90	0.0362	2.95	10.58	9.23	4.69	5.75	0.448

[a] $MeCl_2 = CoCl_2 + NiCl_2$.

TABLE VII. DISTRIBUTION OF COBALTOUS AND NICKELOUS CHLORIDES BETWEEN CAPRYL ALCOHOL AND WATER IN PRESENCE OF HYDROCHLORIC ACID AT 75° C.—SERIES (v)

Mixture No.	Aqueous Phase: $CoCl_2$	$NiCl_2$	$CoCl_2/NiCl_2$	$MeCl_2$[a]	Cl	HCl	Solvent Phase: $CoCl_2$	$NiCl_2$	$MeCl_2$	Cl	HCl	K_{Co}	K_{Ni}	K_{HCl}
	Concentration, Wt. %						Concentration, Wt. %							
Co-Ni-H														
19	5.63	6.12	0.92	11.75	12.1	5.9	0.0100	0.0007	0.0107	0.46	0.47	1.78×10^{-3}	0.11×10^{-3}	0.080
20	5.80	5.98	0.97	11.78	13.0	6.8	0.0133	0.0012	0.0145	0.68	0.69	2.29	0.20	0.102
21	5.31	5.89	0.90	11.20	15.3	9.4	0.0645	0.0040	0.0685	1.44	1.44	1.22×10^{-2}	0.68	0.153
22	5.79	6.28	0.92	12.07	16.2	9.9	0.0965	0.0080	0.1045	2.04	2.04	1.67	1.27	0.206
23	5.21	6.10	0.86	11.31	17.1	11.2	0.136	0.0116	0.148	2.33	2.31	2.61	1.90	0.206
24	5.76	6.33	0.91	12.09	18.7	12.4	0.397	0.0115	0.409	3.74	3.61	6.89	1.82	0.290
25	5.84	6.35	0.92	12.19	20.8	14.5	0.900	0.0179	0.918	5.21	4.85	$.4 \times 10^{-1}$	2.82	0.334
26	6.28	5.83	1.08	12.11	24.5	18.4	2.15	0.0237	2.17	7.80	6.81	.2	4.07	0.371
27	6.75	5.63	1.20	12.38	25.8	19.6	2.53	0.0259	2.56	8.55	7.35	.76	4.60	0.375
28	7.46	5.74	1.30	13.20	26.4	19.7	2.82	0.0266	2.85	8.80	7.45	.50	4.64	0.378

[a] $MeCl_2 = CoCl_2 + NiCl_2$.

TABLE VIII. DISTRIBUTION OF COBALTOUS AND NICKELOUS CHLORIDES BETWEEN CAPRYL ALCOHOL AND WATER IN PRESENCE OF HYDROCHLORIC ACID AT 25° C.—SERIES (vi)

Mixture No.	Aqueous Phase: $CoCl_2$	$NiCl_2$	$CoCl_2/NiCl_2$	$MeCl_2$[a]	Cl	HCl	Solvent Phase: $CoCl_2$	$NiCl_2$	$MeCl_2$	Cl	HCl	K_{Co}	K_{Ni}	K_{HCl}
	Concentration, Wt. %						Concentration, Wt. %							
Co-Ni-H														
29	9.30	8.73	1.06	18.03	25.3	15.9	2.23	0.0289	2.26	9.23	8.23	2.40×10^{-1}	3.32×10^{-3}	0.518
30	7.53	6.36	1.18	13.89	23.5	16.4	1.120	0.0183	1.138	8.00	7.59	1.49	2.88	0.462
31	6.06	4.64	1.31	10.70	21.8	16.4	0.466	0.0130	0.479	6.85	6.78	7.69×10^{-2}	2.80	0.414
32	4.68	3.26	1.44	7.94	20.2	16.3	0.164	0.0081	0.172	5.92	6.00	3.50	2.48	0.368
33	3.09	2.20	1.41	5.29	18.7	16.3	0.057	0.0047	0.062	5.13	5.25	1.84	2.14	0.322
34	1.92	1.38	1.39	3.30	17.4	16.0	0.025	0.0015	0.026	4.38	4.50	1.30	1.1	0.281

[a] $MeCl_2 = CoCl_2 + NiCl_2$.

agree quite well with the values predicted by Figures 2 and 3, respectively.

Practically all of the log K–aqueous chloride concentration curves are linear over part of the experimental range. The curves for cobaltous chloride in the presence of hydrochloric acid are linear up to a value of K of about 0.1. They taper off beyond this point. In contrast, the corresponding nickelous chloride curves show linearity at the higher acid concentrations. When calcium chloride is the added electrolyte, the cobaltous chloride curves are linear for values of K greater than about 0.01. There is a general decrease in slope below this point. The nickelous chloride curves for this added electrolyte show variable linearity characteristics, depending on the cobalt-nickel ratio.

Empirical equations for the linear portions of the curves plotted are presented in Table XIII. The independent variable in each of these equations is not the total chloride concentration but the aqueous phase concentration of the component actually varied. The conditions governing the range of validity of the equations are stipulated. Included in the table are two equations, previously obtained, which apply for extraction of cobaltous and nickelous chloride in the absence of any added electrolyte.

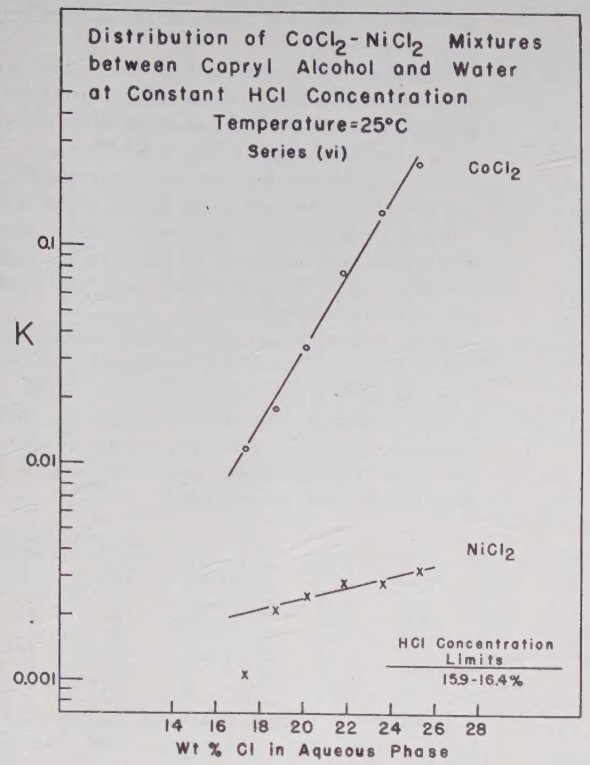

Figure 8

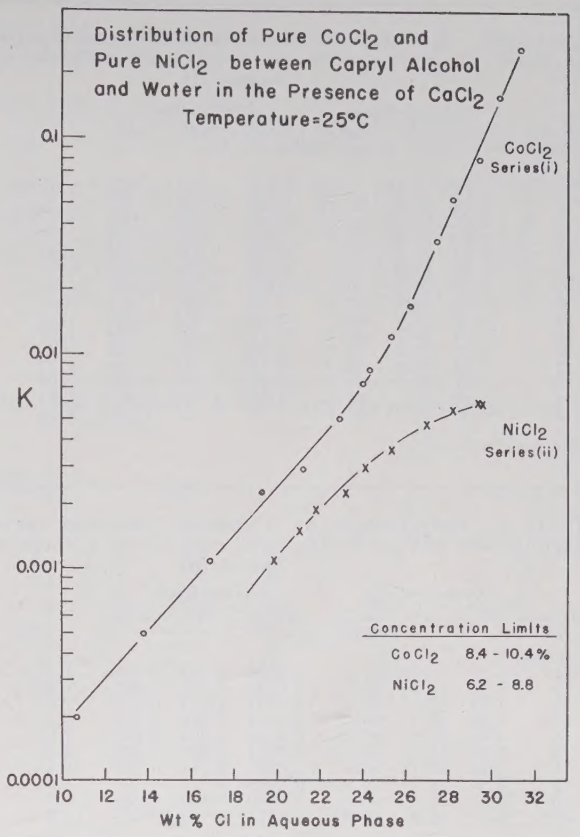

Figure 9

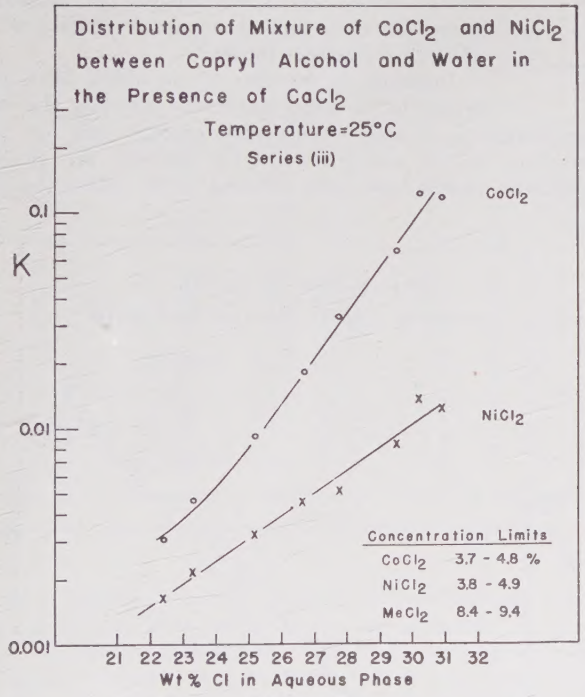

Figure 10

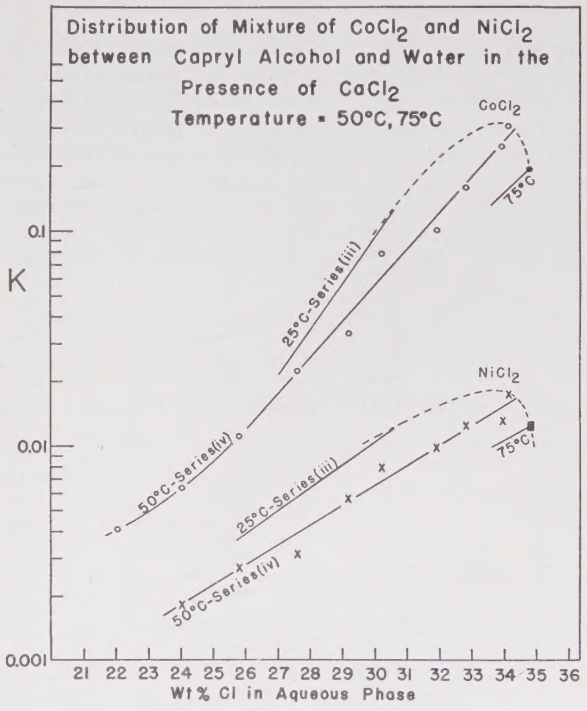
Distribution of Mixture of $CoCl_2$ and $NiCl_2$ between Capryl Alcohol and Water in the Presence of $CaCl_2$
Temperature = 50°C, 75°C
$CoCl_2$
$NiCl_2$
75°C
25°C-Series(iii)
50°C-Series(iv)
K
0.1
0.01
0.001
21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36
Wt % Cl in Aqueous Phase

Figure 11

DISCUSSION

The results show, in support of the qualitative observations originally described (6), that by the addition of either hydrochloric acid or calcium chloride it is possible to produce a remarkable improvement in the extraction of the cobalt salt by capryl alcohol. The change in distribution coefficient obtained with both added electrolytes is of the order of 1000-fold. The nickelous chloride distribution coefficient also increases with added electrolyte content, but much more slowly, and an improved separation thereby results.

The major difference in the effect of hydrochloric acid and calcium chloride addition on the behavior of K_{Co} occurs at high concentrations of the added electrolyte. When hydrochloric acid is used, the log K_{Co} curve tapers off at high acid strengths and the coefficient appears to approach a maximum limit of about 0.5. In concentrated calcium chloride solutions this type of be-